(Aryl)(phosphanyl)Carbene: Ground- and Excited-State Reactions

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Dedicated to Prof. Dr. Wolfgang W. Schoeller on the occasion of his 62nd birthday

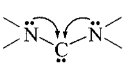
Keywords: Carbenes / Cycloaddition / Diastereoselectivity / Photolysis / Sigmatropic rearrangement

Cyclopropanation, carbene coupling, and photolytically induced 1,2-migration reactions are reported for the stable singlet [bis(diisopropylamino)phosphanyl][*o*,*o*′-bis(trifluoromethyl)phenyl]carbene (**1**).

Introduction

In the last 15 years, our understanding of carbene chemistry has advanced considerably with the preparation of persistent triplet diarylcarbenes[1] and the isolation of singlet carbenes.[2] The first isolated carbenes **A**[3] and **B**[4] featured two heteroatomic substituents that both interact with the carbene center (Figure 1). The range of stable carbenes was recently expanded to include monoheteroatom-substituted carbenes.[5−8] The stabilization modes of the arylcarbenes **1**−**3** differ significantly from one to the other, and the effect of the aryl substituents has been determined recently.[8] According to structural and theoretical analyses, the aryl substituent behaves as an acceptor in **1**,[5] but remains merely a spectator in both carbenes **2**[6] and **3**[7].


A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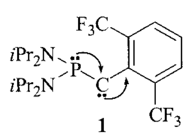
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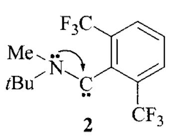
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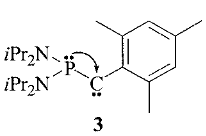
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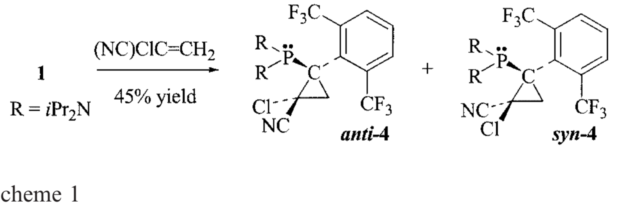
Figure 1. Structure of stable singlet carbenes **A**, **B**, and **1**−**3**

Here we report on the reactivity of the (aryl)(phosphanyl)carbene **1**. Reactions involving the ground state are presented, such as cyclopropanation and carbene coupling reactions. We discuss the electronic effect of the aryl substituent on the chemical behavior of **1**. Isomerization of **1** by a 1,2-sigmatropic shift was observed upon irradiation. This result opens the way for reactions involving the excited states of stable carbenes.

Results and Discussion

First we investigated the chemical behavior of carbene **1** in two typical reactions for transient carbenes, namely cyclopropanation and carbene coupling. At room temperature, no reaction occurs with methyl acrylate, but carbene **1** readily reacts with the more electron-deficient chloroacrylonitrile.[9] Cyclopropane **4** was obtained within a few minutes in 45% yield (Scheme 1). According to ^{31}P and ^{1}H NMR spectroscopy, two isomers of **4** are present in an approximate ratio of 3:1. Colorless single crystals (m.p. 155 °C) were obtained by slow concentration of a saturated diethyl ether solution at room temperature. An X-ray diffraction study (Figure 2) revealed the presence of two diastereoisomers in the same 3:1 ratio,[10] the major product ***anti*-4** featuring the chlorine atom and the phosphanyl group in a *trans* relationship.



Scheme 1

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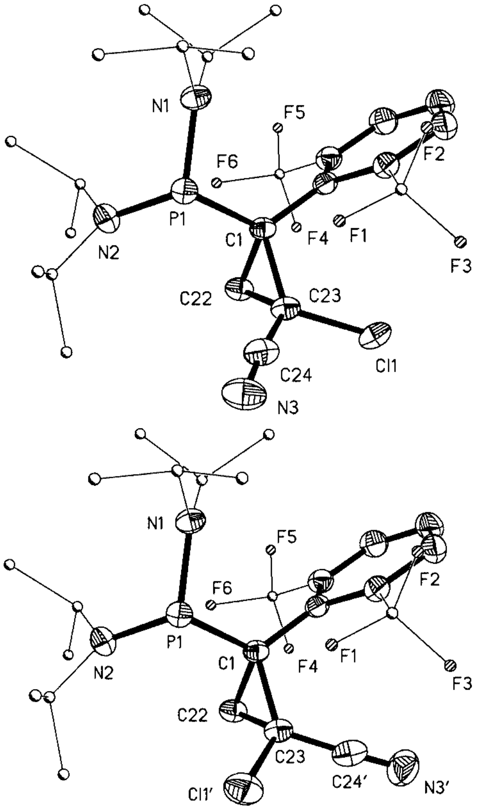
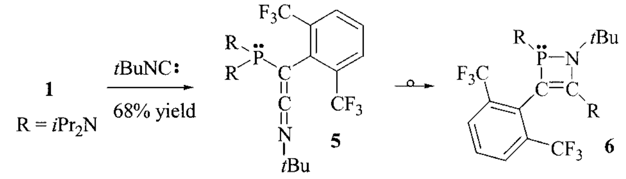


Figure 2. Thermal ellipsoid diagram (50% probability) of ***anti*-4** (top) and ***syn*-4** (bottom); the hydrogen atoms have been omitted and isopropyl groups simplified for clarity; selected bond lengths [Å] and angles [°]: P1−C1 1.968(2), C1−C22 1.517(2), C1−C23 1.555(2), C22−C23 1.493(2), P1−N1 1.697(2), P1−N2 1.700(2); P1−C1−C22 114.14(14), P1−C1−C23 112.81(10), N1−P1−C1 102.56(7), N1−P1−N2 110.78(7), C1−P1−N2 103.87(7)

So far, complete diastereoselectivity has been observed in the reaction of phosphanylcarbenes with alkenes (such as methyl acrylate, styrene, and nonafluorohexene), and this selectivity has been rationalized based on secondary orbital interactions.[11] The formation of both diastereoisomers with chloroacrylonitrile is in perfect agreement with this hypothesis, since both the π bonds of the cyano group and the lone pairs of electrons of the chlorine atom can interact with the carbene vacant orbital.

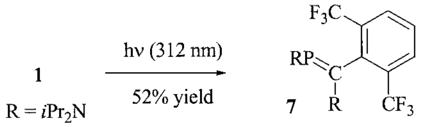
According to previous studies,[8] the *o,o′*-bis(trifluoromethyl)phenyl group exerts only a weak withdrawing effect in phosphanylcarbenes. In fact, it is the steric repulsion between the bulky substituents at the phosphorus center and the aryl ring that widens the carbene bond angle of **1** and thereby induces its push-pull structure. These conclusions are in perfect agreement with the nucleophilicity observed experimentally for **1**.[12]

The chemical behavior of **1** towards alkenes clearly demonstrates its nucleophilic character. Its electrophilic character could only be observed in a carbene coupling reaction. Indeed, **1** smoothly reacts with *tert*-butyl isocyanide at room temperature (Scheme 2). The resulting ketenimine **5** was characterized by ^{31}P NMR ($\delta = 71.6$ ppm, $J_{PF} = 35$ Hz) and IR ($\tilde{\nu} = 2006$ cm^{-1}) spectroscopies. Compound **5** isomerizes slowly at room temperature in solution into the corresponding 1,2-dehydro-1,2-azaphosphete **6**, which was characterized by multi-nuclear NMR spectroscopy. The mechanism for such isomerization processes, exchanging phosphanylketenimines and 1,2-dehydro-1,2-azaphosphetes, has been elucidated recently.[13]



Scheme 2

Thermally induced 1,2-migrations are typical ground-state reactions for transient singlet carbenes,[14] and have recently been observed for persistent (alkyl)(phosphanyl)carbenes.[7] Interestingly, (aryl)(phosphanyl)carbene **1** is stable in toluene solution even after prolonged heating at 80 °C, but readily isomerizes by photolysis in toluene solution at −50 °C. Phosphaalkene **7**, which resulted from the 1,2-migration of an amino group from the phosphorus atom to the carbene center, was isolated in 52% yield (Scheme 3). The isomerization of **1** ($\lambda_{max} = 321$ nm) into **7** occurred only under irradiation ($\lambda = 312$ nm), and thus involved an excited state of carbene **1**, most probably the S_1 or T_1 state featuring singly occupied n_σ and p_π orbitals (Figure 3). It is the first example of an excited-state reaction for a stable carbene, and is reminiscent of that reported in a matrix for the chloro(trifluoromethyl)carbene, which rearranges to the chlorotrifluoroethene upon irradiation at 10 K.[15]



Scheme 3

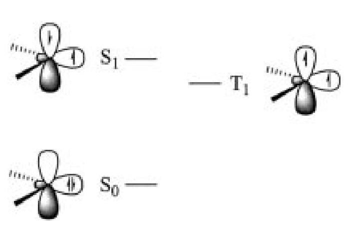


Figure 3. Schematic representation of the ground state and first excited states of singlet carbenes

Conclusion

Although in the solid state the (aryl)(phosphanyl)carbene **1** adopts a cumulenic structure, indicating a push-pull stabilization mode,[5] its chemical behavior towards alkenes clearly demonstrates its nucleophilic character. In other words, the push effect of the phosphanyl group prevails over the pull effect of the aryl substituent. The vacant carbene orbital remains accessible, however, as is shown by the coupling reaction with *tert*-butyl isocyanide. Overall, the reactivity of **1** is very similar to that observed for the previously known (phosphanyl)(silyl)carbenes.

The photolytic isomerization of **1** into **7** is the first example of an excited-state reaction for a stable carbene. Note that similar excited-state reactions of an isolable silylene, the heavier analogs of carbenes, have been reported recently.[16] The isolation of species that have long been considered only as reactive intermediates, even in their ground state, will probably allow for spectacular developments in the understanding of their excited-state behavior.[17]

Experimental Section

General Procedures: All manipulations were performed under argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with Bruker AC200, WM250, and AMX400 spectrometers. ^{1}H and ^{13}C NMR spectroscopic chemical shifts are reported in ppm relative to Me_4Si as an external standard. ^{19}F NMR spectroscopic downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded with a Perkin−Elmer FT-IR 1725 X spectrometer. Carbene **1** was prepared according to a literature procedure.[5]

Cyclopropane 4: An excess of 2-chloroacrylonitrile (0.3 mmol) was added at room temperature to a solution of the [bis(diisopropylamino)phosphanyl][*o,o′*-bis(trifluoromethyl)phenyl]carbene (**1**) (25 mg, 0.06 mmol) in toluene (1 mL). The solvent was evaporated under vacuum, and the residue was washed with pentane and then recrystallized from diethyl ether at room temperature. Yield 14 mg (45%); m.p. 155 °C. ***anti*-4:** ^{1}H NMR (C_6D_6): δ = 1.06 (d, $^{3}J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 1.22 (d, $^{3}J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 1.86 (d, $^{2}J_{H,H}$ = 8.0 Hz, 1 H, CH_{cycle}), 2.73 (dd, $^{2}J_{H,H}$ = 8.0, $^{3}J_{HP}$ = 18.2 Hz, 1 H, CH_{cycle}), 3.63 (m, 4 H, CH), 7.36 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, H_{meta}), 7.42 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, H_{para}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.9 (s, CH_3), 27.2 (s, CH_3), 32.1 (qd, $^{2}J_{C,P}$ = 45, $^{5}J_{C,F}$ = 6 Hz, CH_{2cycle}), 35.2 (m d, $^{1}J_{C,P}$ = 104 Hz, CP), 46.8 (d, $^{2}J_{C,P}$ = 7 Hz, CH), 47.6 (d, $^{2}J_{C,P}$ = 13 Hz, CH), 110.3 (s, CN), 117.9 (d, $J_{C,P}$ = 19 Hz, $C_{arom.}$), 122.0 (d, $J_{C,P}$ = 26 Hz, $C_{arom.}$), 131.9 (d, $J_{C,P}$ = 6 Hz, $CH_{arom.}$), 133.4 (d, $J_{C,P}$ = 4 Hz, $CH_{arom.}$) ppm. ^{19}F NMR (C_6D_6): δ = 23.5 (d, $^{5}J_{FP}$ = 56 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 104.3 (q, $^{5}J_{PF}$ = 56 Hz) ppm. ***syn*-4:** ^{19}F NMR (C_6D_6): δ = 23.4 (d, $^{5}J_{FP}$ = 61 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 106.4 (q, $^{5}J_{PF}$ = 61 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.29 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12 H, CH_3), 1.78 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12 H, CH_3), 2.14 (d, $^{2}J_{H,H}$ = 6.7 Hz, 1 H, CH_{cycle}), 2.37 (dd, $^{2}J_{H,H}$ = 6.7, $^{3}J_{HP}$ = 8.0 Hz, 1 H, CH_{cycle}), 3.15 (m, 4 H, CH), 6.62 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2 H, H_{meta}), 6.68 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, H_{para}) ppm. $C_{24}H_{33}ClF_6N_3P$ (544.0): calcd. C 52.99, H 6.12, N 7.73; found C 52.80, H 5.99, N 7.45.

Ketenimine 5: *tert*-Butyl isocyanide (0.3 mmol) was added at room temperature to a solution of [bis(diisopropylamino)phosphanyl]-[*o,o′*-bis(trifluoromethyl)phenyl]carbene (**1**) (25 mg, 0.06 mmol) in toluene (1 mL). Derivative **5** was characterized spectroscopically without further purification. ^{19}F NMR (C_6D_6): δ = 20.3 (s), 19.8 (d, $^{5}J_{FP}$ = 33 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 71.6 (q, $^{5}J_{PF}$ = 33 Hz) ppm. IR (toluene): $\tilde{\nu}_{CN}$ = 2007 cm^{-1}.

1,2-Dihydro-1,2-azaphosphete 6: A toluene solution of the keteneimine **5** was stirred at room temperature for 3 d. The solvent was evaporated under vacuum to afford derivative **6** as a yellow oil. Yield 20 mg (68%). ^{1}H NMR (C_6D_6): δ = 1.15 (br., 12 H, CH_3), 1.23 (d, $^{3}J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.27 (d, $^{3}J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 1.33 (d, $^{3}J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 1.63 (s, 9 H, CH_3*t*Bu), 3.85 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4 H, CH), 6.52 (pt, $^{3}J_{H,H}$ = 8.0 Hz, 1 H, $H_{arom.}$), 7.59 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1 H, $H_{arom.}$), 7.67 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1 H, $H_{arom.}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 22.0 (s, CH_3), 24.7 (s, CH_3), 30.0 (s, CH_3), 31.3 (d, $^{3}J_{C,P}$ = 12 Hz, CH_3), 32.3 (s, CH_3), 46.5 (s, C*t*Bu), 51.2 (s, CH), 56.3 (d, $^{2}J_{C,P}$ = 8 Hz, CH), 99.4 (d, $J_{C,P}$ = 6 Hz, C_{cycle}), 124.9 (q, $^{1}J_{C,F}$ = 275 Hz, CF_3), 125.2 (q, $^{1}J_{C,F}$ = 275 Hz, CF_3), 125.9 (s, C_{para}), 130.4 (q, $^{2}J_{C,F}$ = 6 Hz, C_{ortho}), 130.8 (q, $^{3}J_{C,F}$ = 6 Hz, CH_{meta}), 131.5 (q, $^{3}J_{C,F}$ = 5 Hz, CH_{meta}), 131.9 (q, $^{2}J_{C,F}$ = 14 Hz, C_{ortho}), 135.0 (d, $^{2}J_{C,P}$ = 12 Hz, C_{ipso}), 156.8 (d, $J_{C,P}$ = 17 Hz, C_{cycle}) ppm. ^{19}F NMR (C_6D_6): δ = 21.3 (s), 20.6 (d, $^{5}J_{PF}$ = 64 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 61.3 (q, $^{5}J_{PF}$ = 64 Hz) ppm. $C_{26}H_{40}F_6N_3P$ (539.6): calcd. C 57.87, H 7.47, N 7.79; found C 57.53, H 7.13, N 7.36.

Phosphaalkene 7: A solution of [bis(diisopropylamino)phosphanyl]-[*o,o′*-bis(trifluoromethyl)phenyl]carbene (**1**, 25 mg, 0.06 mmol) in toluene (1 mL) was irradiated (λ = 312 nm) at −50 °C for 4 d. The phosphaalkene **7** (obtained in 52% yield according to ^{31}P NMR spectroscopy) was characterized without further purification. ^{1}H NMR (C_7D_8): δ = 0.94 (d, $^{3}J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.08 (d, $^{3}J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 1.21 (d, $^{3}J_{H,H}$ = 6.2 Hz, 6 H, CH_3), 3.00 (sept, $^{3}J_{H,H}$ = 6.7 Hz, 2 H, CH), 3.27 (sept, $^{3}J_{H,H}$ = 6.7 Hz, 1 H, CH), 3.48 (sept, $^{3}J_{H,H}$ = 6.2 Hz, 1 H, CH), 6.81 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1 H, H_{para}), 7.44 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2 H, H_{meta}) ppm. ^{13}C{^{1}H} NMR (C_7D_8): δ = 23.2 (d, $J_{C,P}$ = 5 Hz, CH_3), 51.9 (d, $J_{C,P}$ = 7 Hz, *C*HCH$_3$), 124.8 (q, $^{1}J_{C,F}$ = 276 Hz, CF_3), 129.9 (m, $C_{arom.}$), 130.1 (d, $J_{C,P}$ = 7 Hz, $C_{arom.}$), 130.7 (q, $^{4}J_{C,F}$ = 5 Hz,

Table 1. Crystal data and structure refinement for ***syn*-4/*anti*-4**

Empirical formula	$C_{24}H_{33}ClF_6N_3P$
Formula mass	543.95
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.4737(7) Å, α = 81.6310(10)° b = 10.4847(7) Å, β = 72.4450(10)° c = 14.2021(9) Å, γ = 60.0640(10)°
Volume	1288.54(15) Å^3
Z	2
Density (calculated)	1.402 Mg/m^3
Absorption coefficient	0.272 mm^{-1}
F(000)	568
Crystal size	0.5 × 0.5 × 0.6 mm
θ range for data collection	1.50−30.35°
Index ranges	$-9 \leq h \leq 14, -13 \leq k \leq 14, -11 \leq l \leq 19$
Reflections collected	9011
Independent reflections	6737 [*R*(int) = 0.0144]
Completeness to θ	30.35°, 86.9%
Absorption correction	semiempirical
Max./min. transmission	1.000000/0.731818
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	6737/15/352
Goodness-of-fit on F^2	1.204
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0469, wR_2 = 0.1174
R indices (all data)	R_1 = 0.0508, wR_2 = 0.1201
Largest diff. peak/hole	0.438/−0.413 e·Å^{-3}

$CH_{arom.}$), 131.3 (q, $^3J_{C,F} = 3$ Hz, $CH_{arom.}$), 188.1 (d, $^1J_{C,P} = 192$ Hz, C=P) ppm. ^{19}F NMR (C_6D_6): $\delta = 21.6$ (d, $^5J_{FP} = 9$ Hz) ppm. $^{31}P\{^1H\}$ NMR (C_7D_8): $\delta = 172.4$ (m) ppm.

X-ray Crystallography: Data for **4** were collected at low temperature using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. The structure was solved by direct methods using SHELXS-97[18] and refined with all data on F^2 using SHELXL-97.[19] All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined using a riding model. Triclinic, space group $P\bar{1}$; $T = 193$ K; $a = 10.4737(7)$ Å, $b = 10.4847(7)$ Å, $c = 14.2021(9)$ Å; $\alpha = 81.6310(10)$; $\beta = 72.4450(10)$; $\gamma = 60.0640(10)°$; $V = 1288.54(15)$ Å^3; $Z = 2$; R [$I > 2\sigma(I)$] = 0.0469, wR_2 (all data) = 0.1201 for 6737 unique reflections, 352 parameters, GoF = 1.204. CCDC-200073 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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